Indian J. Phys. **80 (1)**, 49-53 (2006)

Investigation of antimony addition on the glass transition kinetics of $Se_{80}Te_{20-x}Sb_x$ using calorimetric measurements

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Received 6 June 2005, accepted 22 November 2005

Abstract : Calorimetric measurements have been performed in glassy alloys $Se_{80}Te_{20}$ and $Se_{80}Te_{20-x}Sb_x$ ($x = 0.5$ and 1) to study the effect of the lower concentration of antimony additive on the kinetics of glass transition in glassy $Se_{80}Te_{20}$ alloy. The variation of T_g with heating rate and composition has also been studied. The heating rate dependence of T_g is used to evaluate the activation energy of glass transition.

The thermal stability of these glasses has also been discussed. It has been found that thermal stability increases on addition of Sb in glassy $Se_{80}Te_{20}$ system. This increase is explained in terms of decrease in activation energy of glass transition.

Keywords : Chalcogenide glasses, differential scanning calorimetry, glass transition kinetics, thermal relaxation.

PACS Nos. : 61.43.Dq, 71.23.Cq, 65.60.+a

1. Introduction

Studies of the chalcogenide glasses in Se-Te-Sb system have received great attention because of their important applications as photoreceptor in xerography and in switching devices [1]. The addition of Sb in Se-Te system modifies considerably the structure of the system. Se-Te-Sb shows memory type switching [2].

One of the most important problems in the area of chalcogenide glasses is the understanding of glass transition kinetics, which can be studied in terms of glass transition temperature T_g, and activation energy of thermal relaxation (E_g). In some of the chalcogenide glassy systems, glass transition temperature T_g is found to vary with the average coordination number. Physical quantities such as, the melting temperature, the magnitude of photo-darkening and width of the band tails in chalcogenide glasses is found to be related with T_g. Therefore, a study of the kinetics of glass transition is one of the most important problems in the area of chalcogenide glasses.

The glass transition is exhibited as an endothermic peak or a shift in the base line in Differential Scanning Calorimetry (DSC) due to change in specific heat. However, in chalcogenide glasses, such an endothermic peak can also be observed due to a fast change in enthalpy when the glassy system relaxes quickly due to a decrease in viscosity at the glass transition temperature. DSC technique can, therefore, be quite useful in the study of thermal relaxation in these glasses.

It has been found by various workers that the structure of glassy Se-Te system is considerably modified by addition of Sb. The effect of Sb on glass transition kinetics in Se-Te system at higher concentration (≥ 1.5) of Sb keeping the Te concentration constant, has been studied by various workers [3–8]. However, no attempt has been made to see the effect of Sb addition on the glass transition kinetics in Se-Te system at lower concentration of Sb (≤ 1.5). Hence, studies on glass transition kinetics and related parameters for Se-Te-Sb

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system are reported here for lower concentration of Sb. Beside this, we have added the Sb in glassy $Se_{80}Te_{20}$ alloy at the cost of Te.

2. Material preparation

Glassy alloys of $Se_{80}Te_{20-x}Sb_x$ (x = 0, 0.5, 1) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Sb elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoules (length ~5 cm and internal diameter ~8 mm). The ampoules containing material were heated to 800°C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3–4°C/minute. During heating, the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules.

3. Experimental techniques

The glassy nature of the alloys was ascertained by X-ray diffraction. The XRD pattern of glassy $Se_{80}Te_{20}$ is shown in Figure 1. Absence of any sharp peak in XRD pattern in Figure 1 confirms the glassy nature of $Se_{80}Te_{20}$ alloy. Similar XRD patterns were obtained for the other two glassy alloys.

The glasses thus prepared, were ground to make fine powder for DSC studies. The thermal behaviour was investigated using differential scanning calorimeter. 10 to 20 mg of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Five heating rates (5, 10, 15, 20 and 25°C/min) were chosen in the present study. Measurements were made under almost identical conditions.

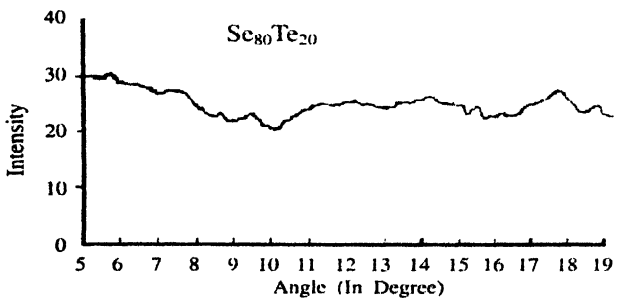

Figure 1. XRD pattern of glassy $Se_{80}Te_{20}$ alloy.

4. Results and discussion

Figure 2 shows typical DSC thermograms at different heating rates for $Se_{80}Te_{19}Sb_1$ alloy. Similar thermograms were obtained for other glassy alloys. It is clear from Figure 1 that well-defined endothermic and exothermic peaks are observed at glass transition temperature T_g and crystallization temperature T_c. The values of T_g at different heating rates for various glassy alloys are given in Table 1.

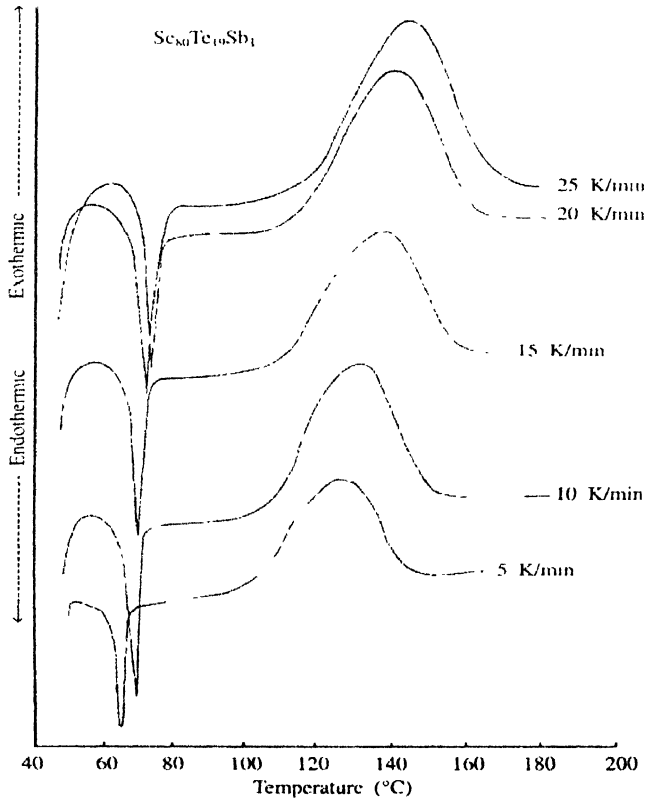

Figure 2. DSC scans of glassy $Se_{80}Te_{19}Sb_1$ alloy for different heating rates.

4.1. Composition dependence of T_g :

The composition dependence of T_g is shown in Figure 3. From Figure 3, it is clear that T_g increases on addition of Sb in glassy $Se_{80}Te_{20}$ alloy. The structure of Se-Te system prepared by melt quenching is regarded as a mixture of

Table 1. Glass transition temperatures of glassy $Se_{80}Te_{20-x}Sb_x$ alloys at different heating rates.

Sample	T_g (K)				
	5 K/min	10 K/min	15 K/min	20 K/min	25 K/min
$Se_{80}Te_{20}$	335	338	341	342	343
$Se_{80}Te_{19.5}Sb_{0.5}$	337	340	342	344	346
$Se_{80}Te_{19}Sb_1$	338	342	345	347	350

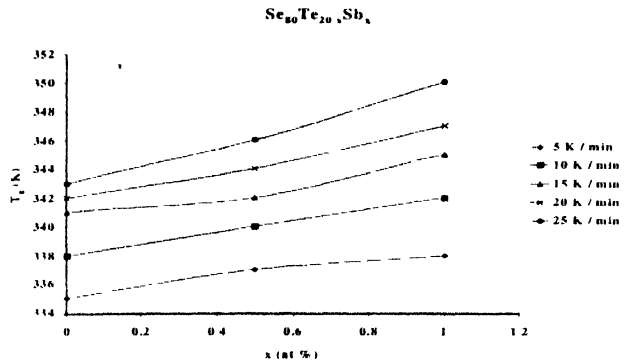

Figure 3. Composition dependence of T_g

Se_8 rings, Se_6Te_2 mixed ring and the Se-Te chains. A strong covalent bond [9] exists between the atoms in the ring, whereas in between the chains, only the Van der Waals forces are dominant. The addition of a small amount of Sb ($\leq$ 1.5) to the Se-Te system leads to its entry into the crosslink chains and hence increasing T_g [6].

The increase in T_g due to addition of Sb in glassy $Se_{80}Te_{20}$ alloy can also be explained in terms of average coordination number (<z>) of glassy $Se_{80}Te_{20-x}Sb_x$ (x = 0, 0.5, 1.0) alloys.

The glass transition temperature T_g of chalcogenide glasses shows dependence on average coordination number <z> [10], which in turn, depends on the percentage of substituent atoms. The variation of T_g with <z> can be expressed as

$$\ln T_g = a\ \langle z\rangle + b. \qquad (1)$$

Above relation is similar to the empirical relation proposed by Tanaka [11]. The plots of ln T_g *vs.* <z> is shown in Figure 4 for the different alloys. The constant 'a' is positive showing the increase of T_g with <z>.

4.2. Thermal stability of glassy $Se_{80}Te_{20-x}Sb_x$ alloys :

The glass transition temperature T_g represents the strength or rigidity of the glass structure in chalcogenide glasses. Hence, T_g affords valuable information on the thermal

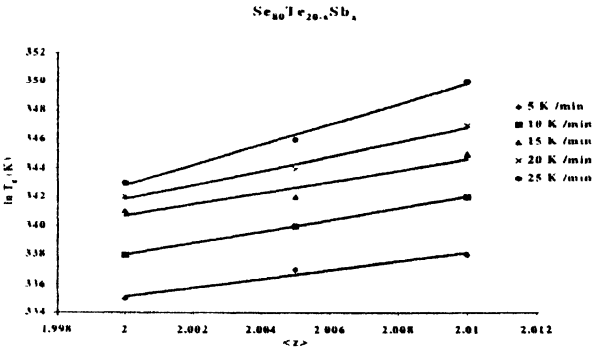

Figure 4. Plots of ln T_g *vs.* <z> for glassy $Se_{80}Te_{20-x}Sb_x$ alloys.

stability of glassy state [12,13] but T_g alone does not give any information on the thermal stability [14]. However, it has been found that the difference of peak crystallization temperature T_c and glass transition temperature T_g is a strong indication of the thermal stability [15]. The higher the values of ($T_c - T_g$), the greater is the thermal stability. The values of T_c and ($T_c - T_g$) at all heating rates are given in Table 2 for different heating rates. It is interesting to note that the value of ($T_c - T_g$) is increased on addition of Sb in binary $Se_{80}Te_{20}$ alloy (see Figure 5)

Table 2 Values of T_c and ($T_c - T_g$) (in K) for ternary alloys at different heating rates

β (K/min)	$Se_{80}Te_{20}$		$Se_{80}Te_{19.5}Sb_{0.5}$		$Se_{80}Te_{19}Sb_1$	
	T_c	$T_c - T_g$	T_c	$T_c - T_g$	T_c	$T_c - T_g$
5	377	42	380	43	399	61
10	384	46	387	47	405	63
15	388	47	392	50	412	67
20	392	50	395	51	417	70
25	395	52	399	53	422	72

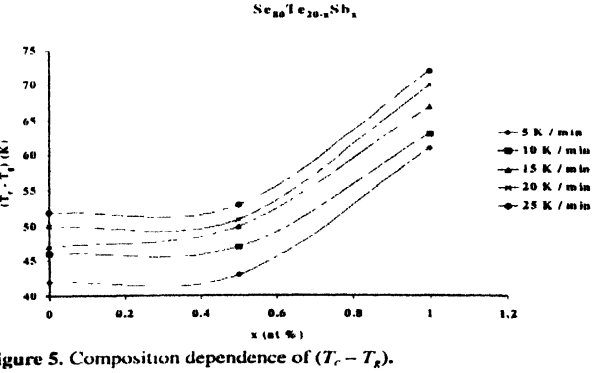

Figure 5. Composition dependence of ($T_c - T_g$).

4.3. Heating rate dependence of T_g :

The glass transition temperature T_g represents the strength

or rigidity of the glassy structure of the alloys. It is well known that T_g of glassy alloys varies with the heating rate β [16–20]. The empirical relation used to analyze the dependence of T_g on β is of the form :

$$T_g = A + B\log, \quad (2)$$

where A and B are constants.

The value of A indicates the glass transition temperature for the heating rate of 1 K/min. It has been found by various workers that the slope B in the eq. (2) is related to the cooling rate of the melt : the lower the cooling rate of melt, the lower the value of B. The physical significance of B seems to be related with the response of the configurational changes within the glass transformation region. The plot of T_g *vs.* log β for the present glassy alloys is shown in Figure 6. The values of A and B for different alloys are given in Table 3. The values of B for all the glassy alloys have been found to be different, indicating that these glassy alloys undergo different structural changes. The results shown in Table 3 indicate the validity of this relationship for the present glassy alloys.

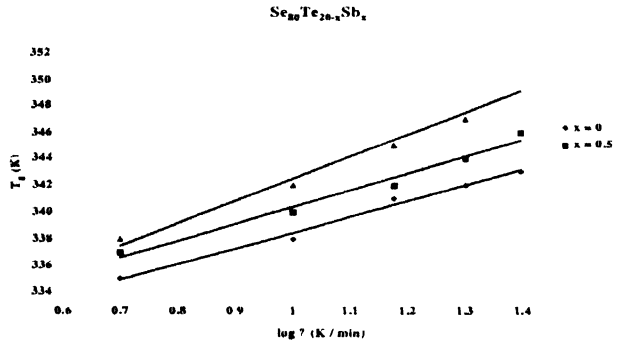

Figure 6. Plots of T_g *vs.* log β for glassy $Se_{80}Te_{20-x}Sb_x$ alloys.

Table 3. Values of E_g, A and B of glassy $Se_{80}Te_{20-x}Sb_x$ alloys.

Sample	E_g (kJ/mol)		A (K)	B (min)
	Eq. (3)	Eq. (4)		
$Se_{80}Te_{20}$	178.8	184.5	326.7	11.8
$Se_{80}Te_{19.5}Sb_{0.5}$	168.8	174.5	327.8	12.5
$Se_{80}Te_{19}Sb_1$	146.9	152.6	325.9	16.5

4.4. Evaluation of activation energy of glass transition (E_g) :

The activation energy of glass transition (E_g) can be evaluated using the use of the Kissinger's linear dependence [21] in the form :

$$\ln (T_g^2)/\beta = E_g/RT_g + \text{constant}. \quad (3)$$

In addition, when the variation of $\ln(1/T_g^2)$ with $\ln \beta$ is much slower than that of $1/T_g$ then eq. (3) converts in to the form [22] :

$$\ln \beta = -E_g/RT_g + \text{constant}. \quad (4)$$

The plots of $\ln (T_g^2)/\beta$ and $\ln \beta$ against $10^3/T_g$ are shown in Figure 7. Using the slopes of these plots, the activation energy of the glass transition process is calculated for the various alloys and is given in Table 3. It is clear from this table that the E_g values are in good agreement with each other. This shows that one can use any of the eqs. (3) and (4) for the evaluation of E_g.

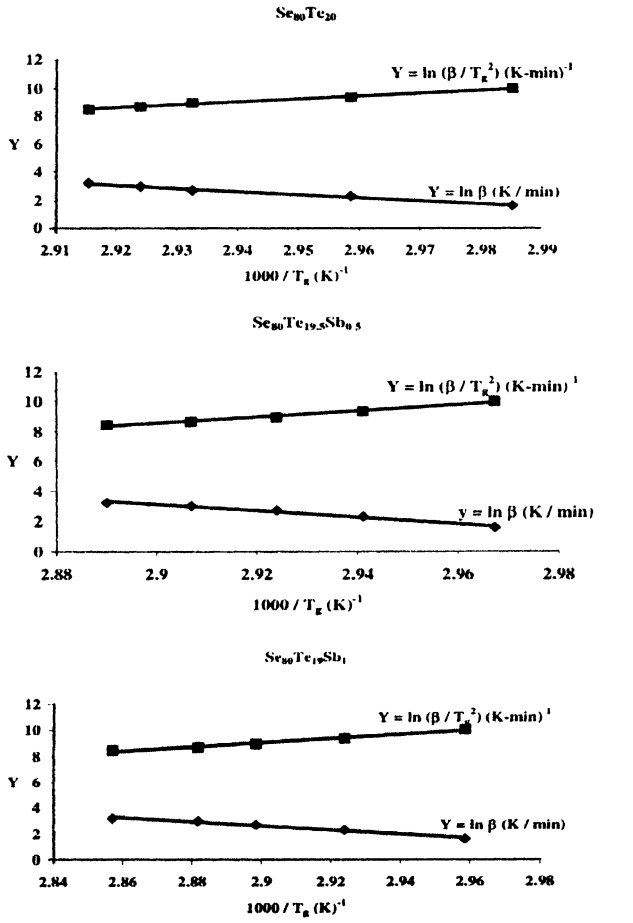

Figure 7. Plots of $\ln \beta$ and $\ln (\beta/T_g^2)$ *vs.* $1000/T_g$ for glassy $Se_{80}Te_{20-x}Sb_x$ alloys.

From Table 3, it is clear that E_g decreases on addition of Sb in binary $Se_{80}Te_{20}$ alloy. The glass transition activation energy is that amount of energy, which is absorbed by a group of atoms in the glassy region so

that a jump from one metastable state to another is possible. This means that E_g is involved in the molecular motions and rearrangements of atoms in the glass transition region. When the sample is heated in DSC furnace, the atoms undergo infrequent transitions between the local potential minima separated by different energy barriers in the configuration space, where each local minimum represents a different structure. The most stable local minimum in the glassy region has lower internal energy. Accordingly, the atoms in the glass having minimum activation energy have higher probability to jump to the metastable state (or local minimum) state of lower internal energy and hence, are the most stable. In the glassy $Se_{80}Te_{20-x}Sb_x$ (x = 0, 0.5, 1) system, E_g increases in the sequence $(E_g)_{x=1} < (E_g)_{x=0.5} < (E_g)_{x=0}$, which indicates that thermal stability of glassy $Se_{80}Te_{20}$ alloy is increased on addition of Sb. This is also confirmed from the value of $(T_c - T_g)$ for the present alloys, which increases in the sequence $(T_c - T_g)_{x=0} < (T_c - T_g)_{x=0.5} < (T_c - T_g)_{x=1}$. Hence, one can conclude that the activation energy of glass transition process is related to thermal stability in the present glasses. Higher thermal stability may require less activation energy for glass transition process as found in the present study. This is confirmed from the plots of E_g vs. $(T_c - T_g)$ at all the five heating rates [see Figure 8]. Similar relation between E_g and $(T_c - T_g)$ have been reported by Mehta *et al* [23] in case of $Se_{70}Te_{20}M_{10}$ (M = Ag, Cd, Sb) alloys.

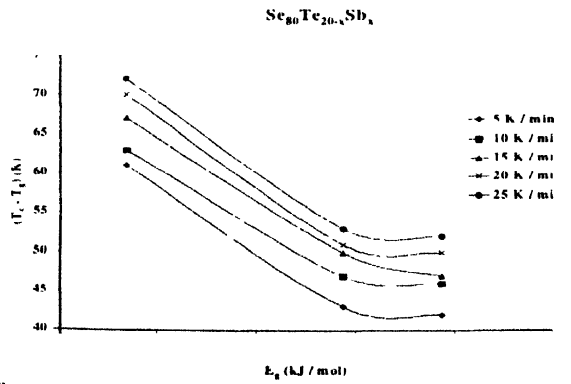

Figure 8. Plots of E_g vs. $(T_c - T_g)$ for glassy $Se_{80}Te_{20-x}Sb_x$ alloys at different heating rates.

5. Conclusions

Calorimetric measurements have been performed in glassy $Se_{80}Te_{20-x}Sb_x$ alloys (x = 0, 0.5, 1.0). DSC scans of these alloys show the well-defined endothermic peak at glass transition temperature (T_g). It has been found that the glass transition temperature increases with increase in the concentration of Sb. This increase in T_g of ternary alloys is explained in terms of cross-linking of Sb in Se-Te chains in these alloys.

In the present work, the significant variation has been found in the activation energy of glass transition and thermal stability even at low concentration of the Sb additive. The activation energy of glass transition process (E_g) is found to be related with $(T_c - T_g)$ in reverse sequence. Hence, one can conclude that the activation energy of glass transition process is related to thermal stability in the present glasses. The glasses having higher activation energy for glass transition process shows less thermal stability.

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